

Interaction of Indenopyridines with [60]-fullerene: A spectroscopic and computational study

Chiranjit Pal^a, Tandrima Chaudhuri^b*, Chhanda Mukhopadhyay^c & Manas Banerjee^d

^aDepartment of Chemistry, Ramananda College, Bishnupur, Bankura 722 122, India

^bDepartment of Chemistry, Dr. Bhupendranath Dutta Smriti Mahavidyalaya, Burdwan 713 407, India

^cDepartment of Chemistry, University of Calcutta, 92 APC Road, Kolkata 700 009, India

^dDepartment of Chemistry, University of Burdwan, Burdwan 713 104, India.

Email: tanchem_bu@yahoo.co.in

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Heterocyclic polynuclear planar indenopyridines (I1, I3 and I4) revealed superior wrapping of [60]-fullerene and formed stable ground state equilibrium defined via formation of absorption isosbestic and isoemissive as well. All three indenopyridines showed almost similar order of ground state formation constant both in Benesi-Hildebrand and in Stern-Volmer methods with [60]-fullerene in toluene medium. Density functional theory (DFT) based computation warranted the experimental finding in terms of loss of planarity of indenopyridines, FMO features to define electron donor and acceptor, electrochemical indices to affirm the direction of electron swing and finally time dependent density functional theory (TD-DFT) calculation showed that HOMO to (LUMO+2) has been found to be the most pronounced transition for the strongest binding with I4.

Keywords: Indenopyridines, Fullerene, Isosbestic formations, Density functional theory, Electrochemical indices

Different aspects of donor-acceptor interaction between fullerene and aromatic hydrocarbons have already been studied¹⁻⁵. Ogilby *et al.*, reported a very weakly bound ground-state CT complex with a small equilibrium constant of 0.08 M⁻¹ for the [60]-fullerene-1-methyl naphthalene complex in toluene¹. Sibley *et al.*, reported formation constant (K) = 0.1 M⁻¹ for the [60]-fullerene-naphthalene complex and increasing values slightly as the number of the aromatic rings of the donor is increased². Bhattacharya *et al.*, reported the interaction of both [60]- and [70]-fullerene-polycyclic aromatic hydrocarbons in carbon tetrachloride medium by ¹H NMR study^{3,5}.

Indenopyridine like planar N-containing polynuclear aromatic compounds exhibit significant chemical and biological importance and behave as good electron donors in the presence of an acceptor⁶⁻⁹. Our previous works show that Indenopyridines are as efficient as polynuclear aromatic hydrocarbons like naphthalene and anthracene, to donate electron and form a weak binding complex with (dibenzoylmethanato) borondifluoride^{8,9}. To the best of our knowledge, there is no report of its interaction with any of the fullerene-like electron acceptors till date. So the purpose of this study is to investigate the

mode and efficiency of interaction of indenopyridine donors with [60]-fullerene acceptor. To examine whether the weakly bound adduct of fullerene-indenopyridine system may be useful as electron or energy transfer device, both spectroscopic and DFT based computational study have been investigated and reported in detail. In this study the formation of reaction equilibrium between [60]-fullerene and three different indenopyridines viz., I1, I3 & I4 (Supplementary Data, Fig. S1) are well established via the formation of both absorption isosbestic and isoemissive in toluene medium. Furthermore the interaction in the complex was modelled with DFT based global minimum geometry change, FMO features, electrochemical indices and finally by TD-DFT calculations.

Materials and Methods

Toluene used as solvent was of HPLC (Merck India) grade. Indenopyridines (I1, I3 & I4) used were prepared according to the reported methods¹⁰⁻¹¹. The [60]-fullerene was purchased from Sigma Aldrich. The concentration of Indenopyridines (I1, I3 & I4) was taken in the range of 10⁻⁵ M–10⁻⁶M and [60]-fullerene was taken in micro molar range in all the spectral measurements.